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RESULTS OF THE MEASUREMENT OF ATMOSPHERIC OZONE  
AND HYDROCARBONS IN BADEN-WÜRTTEMBERG

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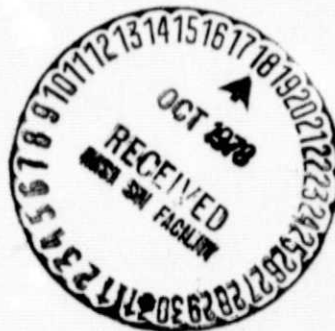
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# RESULTS OF THE MEASUREMENT OF ATMOSPHERIC OZONE HYDROCARBONS IN BADEN-WÜRTTEMBERG

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## 1. Measurement Points and Analysis Method

Ozone along with other components was measured in automatic multi-component test stations in Baden-Württemberg [1]. We do not assume that the values measured in this program permit fundamental new findings, especially since daily and annual variations in ozone as a function of time and solar irradiation can be assumed to be general knowledge and have already been discussed in detail at the 1974 Colloquium on Nitrogen Oxides. For this reason the article focuses on the comparability of the measured values obtained at the individual stations and, in keeping with the theme, no attempt is made to interpret the individual test values. /57\*

Ozone concentration was measured at the test stations of the Baden-Württemberg automatic multi-component immission measurement system in central, southern and northern Mannheim since January 1975 and central and west Karlsruhe since January 1976.

Chemilluminescence gas analyzers made by Bendix Co. were used to measure the ozone concentration. Calibration was done automatically in a 25-hour cycle by means of a built-in test gas source. The concentration of the test gas source was tested afterwards chemically as per VDI 2468 page 1 (KJ method).

The samples for the hydrocarbon immission measurements were taken from the third story of the Regional Agency for Environmental Protection about 800 meters from the west Karlsruhe

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\* Numbers in the margin indicate pagination in the foreign text.

measurement station. A U 180 environmental chromatograph was used to measure the hydrocarbon immission concentration [2].

The mass hydrocarbon concentration in 1.2 liters of atmospheric air was concentrated in a storage column, cooled to  $-30^{\circ}\text{C}$  and separated at  $60^{\circ}\text{C}$  in an isothermal chromatograph.

Cycle time	15 min
Storage time	12 min
Storage column	15 cm/3 mm Spherosil XOA 400 and CMS B
Preseparation column	50 cm Poropak S
Separation columns	50 cm Poropak T + S
Carrier gas	Oxygen 25 ml/min

Backwashing was done after elution of acetylene from separation column A. Evaluation is done by peak surface comparison.

A test gas consisting of

0.39 ppm  $\text{C}_2\text{H}_6$   
0.82 ppm  $\text{C}_2\text{H}_4$  and  
2.35 ppm  $\text{C}_2\text{H}_2$

was used to calibrate the measured components ethylene, ethane and acetylene. The test gas mixture was diluted with synthetic air through microapertures to concentrations between 0.9 ppb and 400 ppb and delivered to the intake point of the chromatograph, i.e. under the same conditions as atmospheric air. The concentration of the test gas mixture was determined by dilution of ethylene and ethane (Schuchard, degree of purity 99.5%) through microapertures. The acetylene concentration of the test gas was determined by means of the response factor.

Table 1 lists the characteristic process quantities of the system. The mean standard deviation around the regression line in the range of 0.9-400 ppb turned out to be 0.9 ppb for ethylene and ethane and 3.2 ppb for acetylene.

Table 1. Characteristic process quantities as per VDI 2449.

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	$Mb$ ppb	$\sigma^*$ ppb	$\sigma$ ppb	$U(195.6)$ ppb	$R$	$z$	$n$	Nachweisgrenze ppb $\Delta$
$C_2H_6$	0.9-314.5	0.9		154		8	24	0.3
	- 2		0.1	0.29	6.85	1	3	
	- 10		0.24	0.48	20.68	1	6	
	- 314.5		4.88	30.81	10.19	1	2	
$C_2H_4$	1.9-398	0.9				7	22	0.2
	- 4		0.166	0.39	10.26	1	4	
	- 10		0.42	0.89	11	1	6	
	- 20		0.59	1.39	14.4	1	4	
	- 90		0.65	4.1	21.9	1	2	
	- 110		5.11			1	2	
$C_2H_2$	5.6-312	3.2				4	11	0.3
	- 30		0.7	1.41	21.3	1	6	
	- 50		0.38	0.89	5.59	1	4	
	- 250		0.43	2.72	32.1	1	2	

Key: A. Detection limit

## 2. Daily Variation and Average Daily Variation in Ozone Concentration

Fig. 1 shows the average daily variation in ozone concentrations for the Mannheim south, Mannheim center and Karlsruhe west stations for the month of June. All three stations show the familiar daily variation in ozone concentration. The concentration increases in the morning, reaches its maximum in early afternoon and then decreases again towards evening. If, by contrast, we examine the concentration curve on an individual day, it turns out that differences in ozone concentration both with regard to place and time occur between the stations. As an example, Fig. 2 shows the daily variation in ozone concentration on June 23, 1976, at the Mannheim center and Karlsruhe west



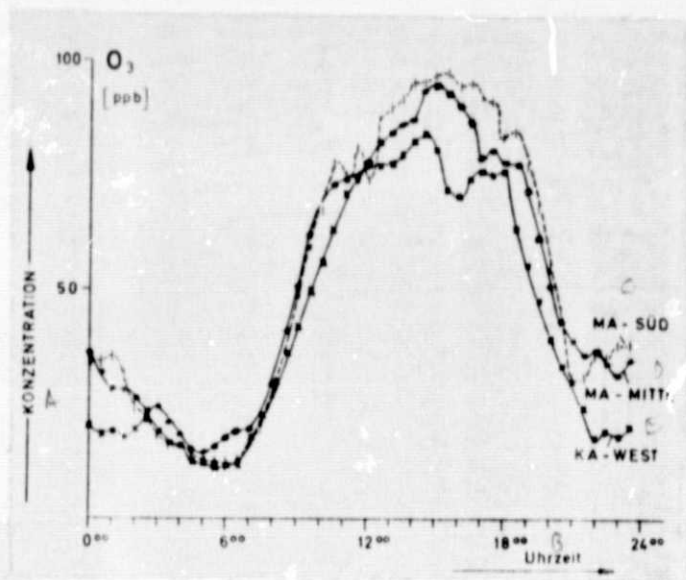


Fig. 1. Daily variation from the mean value a.T. [expansion unknown] of the  $O_3$  concentration, June 1976.

Key: A. Concentration  
 B. Time  
 C. Mannheim south  
 D. Mannheim center  
 E. Karlsruhe west

At the Mannheim center station the ozone concentration increases substantially more sharply than at the Karlsruhe West station. The ozone concentration in Karlsruhe reaches its maximum as early as 1:00 p.m., and in Mannheim the ozone concentration continues to increase and reaches its maximum only around 2:30 p.m. The maximum ozone concentration in Karlsruhe was  $270 \mu\text{g}/\text{m}^3$  and  $664 \mu\text{g}/\text{m}^3$  in Mannheim center. This value was the greatest half hour mean value measured in this year.

Fig. 3 shows the cumulative frequency of ozone concentration at the Mannheim Center, Karlsruhe Center and Karlsruhe West stations for June 1976. The almost identical curves suggest a uniform source distribution at all of the stations. The 50% value of the cumulative frequency lies around  $70 \mu\text{g}$  of ozone per cubic meter, the 95% value around  $300 \mu\text{g}$  per cubic meter. The Mannheim South and Mannheim North stations show the same cumulative frequency and were not included here only to keep the presentation simple.

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Bild 1. Tagesgang aus MW a.T. der  $O_3$ -Konzentration, Juni 76

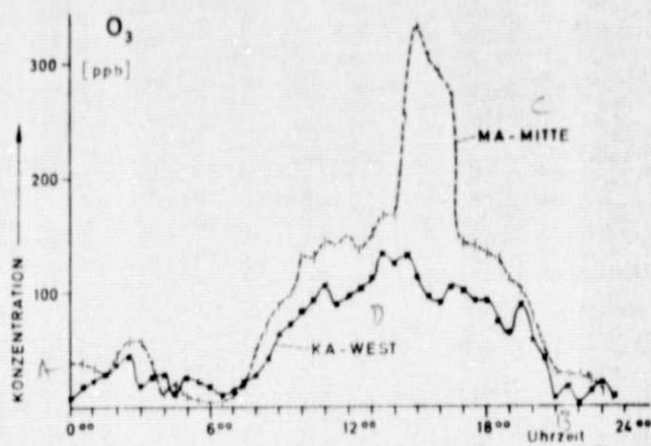


Fig. 2. Daily variation in  $O_3$  concentration on June 23, 1976.

Key: A. Concentration  
B. Time  
C. Mannheim center  
D. Karlsruhe west

1976,  $20 \mu\text{g}/\text{m}^3$  in December 1975; this corresponds to the 6.5-fold portion of the month of June. The 95% value turned out to be  $270 \mu\text{g}/\text{m}^3$  in June 1976 and  $23 \mu\text{g}/\text{m}^3$  in December 1976.

The annual mean values for August 1975 to July 1976 were as follows:

Mannheim South	$41 \mu\text{g}/\text{m}^3$
Mannheim Center	$33 \mu\text{g}/\text{m}^3$
Mannheim North	$35 \mu\text{g}/\text{m}^3$ .

Fig. 4 shows the seasonal dependency of the mean daily variation of ozone. The months of September and December 1975, January, April and July 1976 were selected for this. While in spring and autumn the mean daily variation resembles that of the summer months, the mean daily variation in ozone concentration in the winter months does not show any pronounced maximum. The cumulative frequency of the ozone concentration for December 1975 and June 1976 at the Mannheim center test station is shown in Fig. 5. The 75% value for ozone was  $130 \mu\text{g}/\text{m}^3$  in June

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Bild 2. Tagesgang der  $O_3$ -Konzentration am 25.6.76

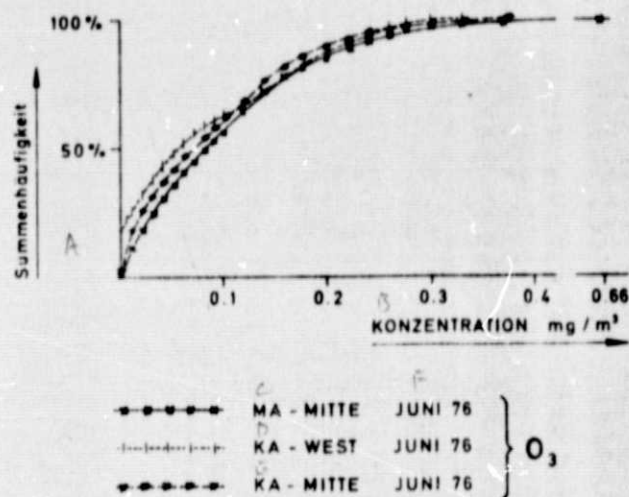


Fig. 3. Cumulative frequency of the  $O_3$  concentrations.

Key: A. Cumulative frequency  
B. Concentration  
C. Mannheim center  
D. Karlsruhe west  
E. Karlsruhe center  
F. June

The 95% values were:

Mannheim South	166 $\mu\text{g}/\text{m}^3$
Mannheim Center	170 $\mu\text{g}/\text{m}^3$
Mannheim North	144 $\mu\text{g}/\text{m}^3$ .

The results show that the annual mean values and the mean daily variations in ozone concentration for one month at the Mannheim and Karlsruhe stations are comparable both in terms of concentration and variation in concentration. By contrast, the variation in concentration and concentration itself on individual days can differ considerably in Mannheim and Karlsruhe.

### 3. Average Daily Variation of Ethane, Ethylene, Acetylene and Ozone in August 1976

Fig. 6 shows the average daily variation in ethylene, ethane, acetylene and ozone concentrations in August 1976. Here only the average daily variation for ozone corresponded to the expected variation.

Ethane shows no pronounced daily variation; a slight drop can be observed only in the late afternoon.

The graphs for acetylene and ethylene run in parallel during low ozone concentrations, i.e. during nighttime hours. Both of them climb to about twice the concentration with the beginning



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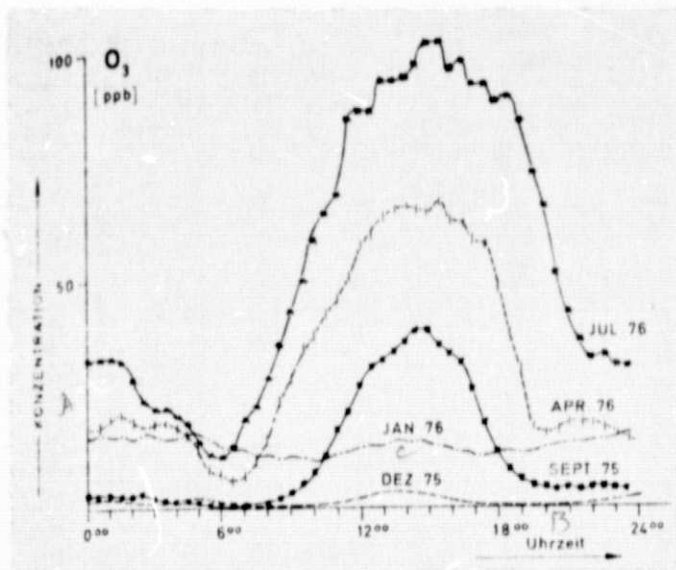


Fig. 4. Daily variation from the mean value a.T. [expansion unknown] of the  $O_3$  concentration, Mannheim south.

Key: A. Concentration  
B. Time  
C. Dec.

of commuter traffic. With increasing ozone concentration the acetylene concentration decreases. The acetylene concentration reaches its minimum when the ozone concentration is at a maximum. With the late afternoon or going home traffic--3:30-6:30--the acetylene concentration increases only slightly. Only after 6:00 can a sharp increase be seen, which reaches its maximum at about 10:00.

Ethylene shows a completely different graph during the daytime hours. After an increase in the morning the ethylene

concentration fluctuates strongly without a recognizable trend. Only in the afternoon, about one and a half hours before the ozone, does the ethylene concentration fall in parallel with the ozone concentration. After passing through the minimum at about 6:00 the ethylene concentration again rises in parallel with acetylene. The monthly mean values were as follows: /60

	$\bar{c} \text{ } \mu\text{g}/\text{m}^3$	$c_{95\%} \text{ } \mu\text{g}/\text{m}^3$
Ethane	2.7	2.5
Ethylene	11.2	18.8
Acetylene	8.6	12.2

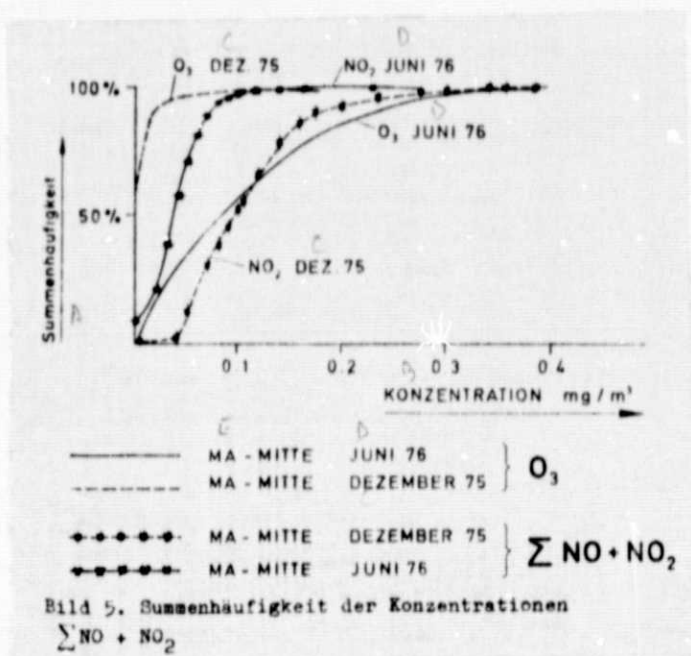


Fig. 5. Cumulative frequency of the concentrations  $\Sigma \text{NO} + \text{NO}_2$ .

Key: A. Cumulative frequency  
B. Concentration  
C. December  
D. June  
E. Mannheim center

In our opinion, a conclusive interpretation of the daily variation or a clarification of the relationship between ozone and hydrocarbons is not possible, since the collective measured values to be sure are representative for the month of August, but the average daily variation for one month does not allow any inferences as to interrelationships. Although a connection between acetylene and ozone is obvious, a decomposition of acetylene by ozone is to be ruled out, since alkynes are substantially slower to react than alkenes during ozonolyses [3].

If we assume automobile traffic to be a ground-level source of acetylene and ethylene, then the counter movement of the acetylene concentration in comparison to the ozone concentration might be attributed to the occurrence of exchange reactions. However, since acetylene and ethylene are emitted by automobiles in a 1:1 ratio and the ethylene concentration does not follow the acetylene concentration curve, a ground-level source for ethylene has to be ruled out as the sole emittent. To explain the lack of a drop in ethylene concentration a high source must also be taken into consideration. However, an examination of

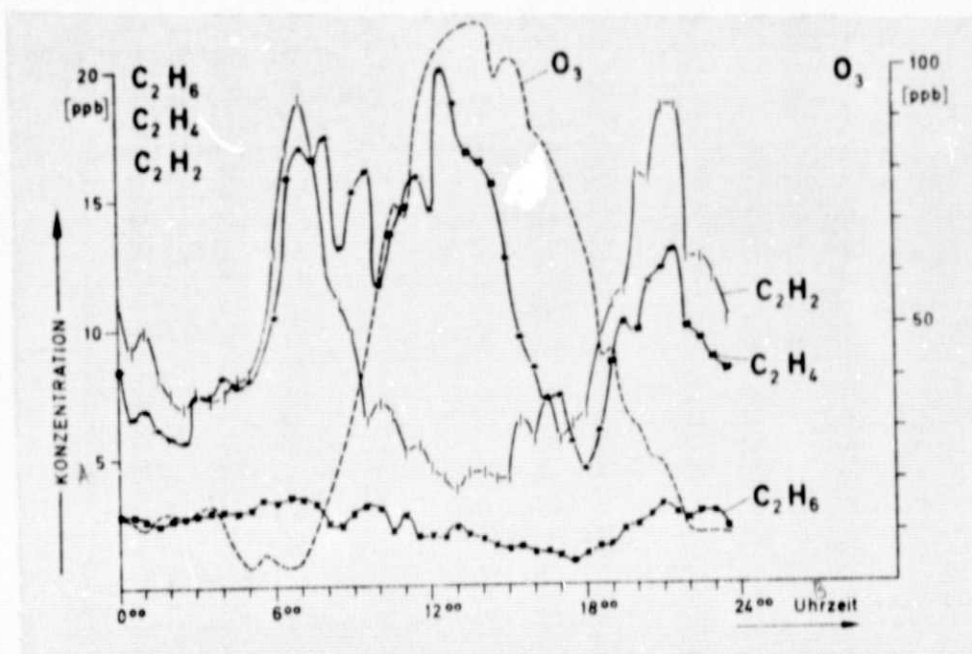


Fig. 6. Daily variation from the mean value a.T [expansion unknown] for C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and O<sub>3</sub>, August 1976, LfU 2 OG.

the frequency distribution on 2 maximums do not result in conclusive confirmation.

#### Appendix

Based on an agreement between Mr. Siegel, M.S. Chemistry, and Prof. Becker of Bonn/Wuppertal of September 27, 1976, on October 8, 1976, an ozone monitor (Bendix, model 8002) of the Baden-Württemberg measurement network at the Mannheim Center test station was calibrated by colleagues of the Institute for Physical Chemistry, Bonn University, using a basic absorption spectroscopy process. Up to this time the ozone measurement instruments in Mannheim had been calculated exclusively using the KJ method.

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The control calibration was done with a device brought from Bonn for calibrating ozone analyzers by measuring the optical absorption (cf. Staub-Reinhaltung der Luft, 35, 326 (1975)). Oxone-containing test gas was produced from synthetic air with a photochemical ozone generator which was also brought from Bonn and conveyed to the ozone monitor through the optical measurement cell of the calibration system. Fig. 7 shows the results of the measurements. Here the ozone concentrations indicated by the Bendix ozone monitor were plotted against those /61 measured in the calibration system.

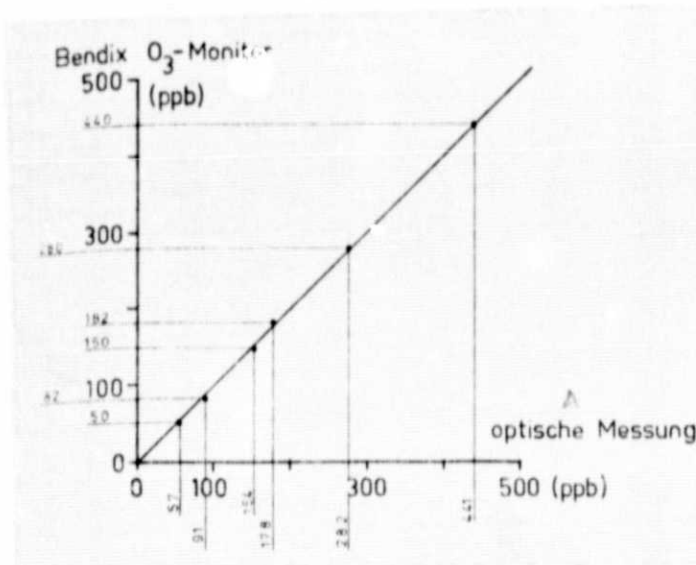


Fig. 7. Reference calibration.  
Key: A. Optical measurement

The averaging line through the measured points reveals excellent agreement between the O<sub>3</sub> concentrations measured by absorption optics and those indicated by the Bendix monitor.